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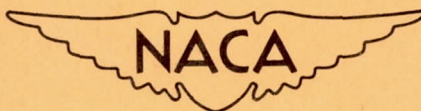
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3279

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PARTS EXPOSED TO FLAME ENVIRONMENTS

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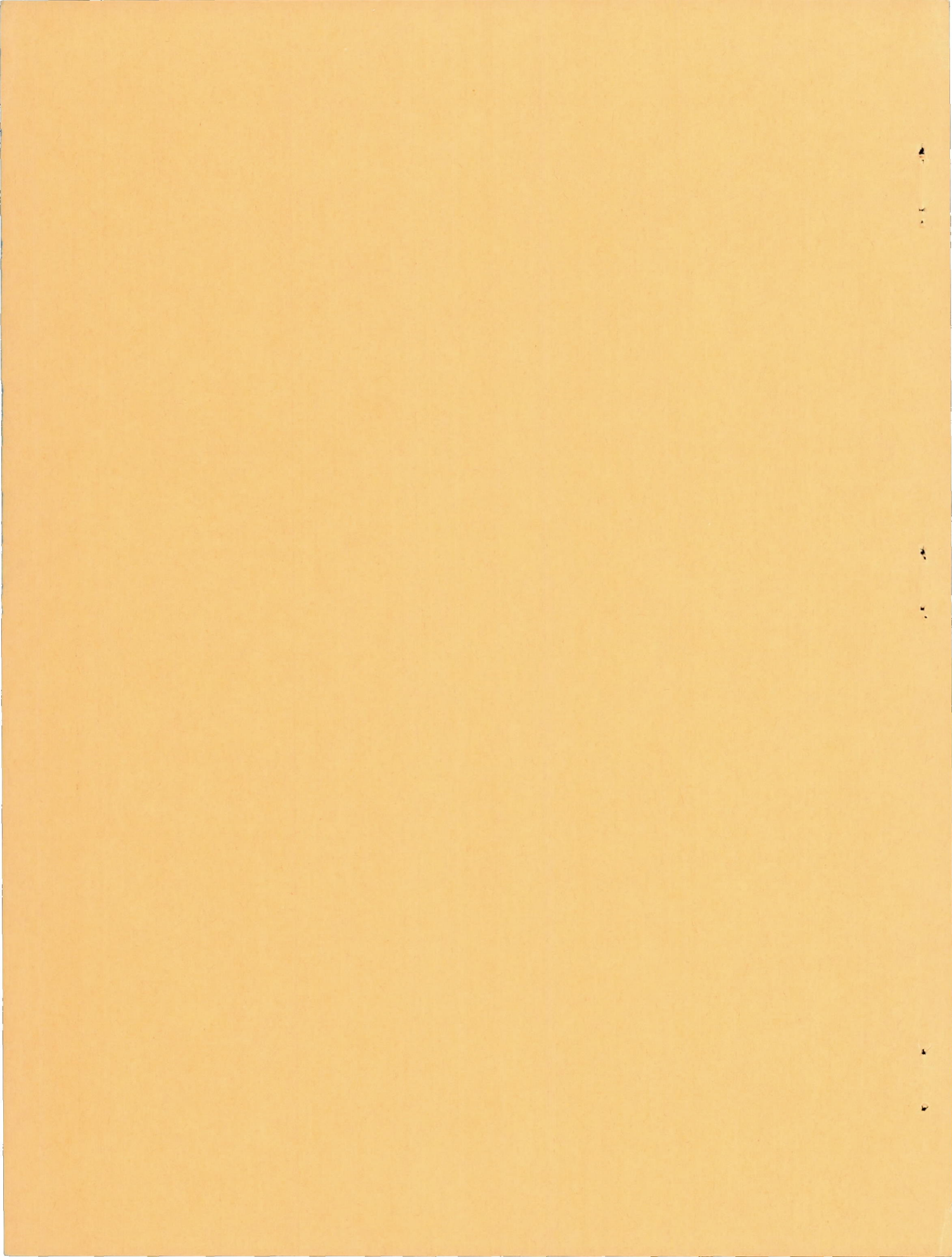
Lewis Flight Propulsion Laboratory
Cleveland, Ohio



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SUMMARY

The effect of phosphate coatings on the temperature of metal specimens placed in a flame was investigated. Since flames contain large numbers of atoms and radicals that react on metal surfaces liberating heat, it was thought that a phosphate coating might decrease the temperature of the metal by poisoning the surface to these reactions.

Small cylindrical specimens of mild steel and S-816 alloy were placed in a natural-gas - air flame. For mild steel, uncoated specimens attained a temperature of 1900° F. This temperature remained constant, apparently because of lack of oxidation of the steel by the flame gases. Phosphated specimens attained a temperature nearly 200° F lower. For S-816 alloy, uncoated specimens reached a temperature of 1900° F, but the temperature fell to 1750° F, dropping rapidly at first and then gradually. This drop was apparently due to oxidation of the specimens. Phosphated specimens attained a temperature about 100° F lower which was maintained even after 300 hours in the flame.

A phosphate coating on S-816 alloy reduced the surface recombination of either hydrogen or oxygen atoms by a factor of $1/3$. However, the oxide surface formed on S-816 alloy in the flame reduced these recombinations by a factor of $2/3$. This result, along with evidence from emittance measurements, indicates that the temperature lowerings obtained in the flame by phosphating the surface arise primarily from the high emittance of the phosphate coating rather than from a poisoning action.

The phosphate coatings appear to have a high emittance, close to 1, and it is suggested that they might have an application on the outer surface of combustor cans.

INTRODUCTION

It is generally accepted that flames contain large numbers of very active particles, such as atoms and free radicals (ref. 1). Also, it is known that the surfaces of most metals act as efficient catalysts for the recombination and reaction of these particles (ref. 2, pp. 317-321). Such reactions are highly exothermic, and significant quantities of heat may thus be imparted to metals exposed to flame environments (ref. 1, p. 168). In jet-engine components this heating is undesirable.

Studies of heterogeneous catalysis (ref. 2, pp. 270-273) have shown that certain elements, such as arsenic, phosphorous, and sulfur, poison most metal surfaces when present on them, that is, prevent reactions from occurring on the metal surfaces. Consequently, it was thought that phosphating of metal surfaces exposed to flame environments might effect a reduction in the temperature of the metal. Phosphate coatings can be produced by well-known procedures on a production basis. In addition, they are strongly adherent and relatively stable to heat.

The purpose of this research was twofold: first, to discover if phosphate coating of metals lowered the temperature of the metals when exposed to a flame environment and second, if a temperature lowering were effected, to determine the mechanism of the lowering. The results are therefore presented in two parts.

DETERMINATION OF TEMPERATURE LOWERING

Coatings

The effect of phosphate coatings on SAE 1020 mild steel and S-816 alloy was studied. The mild steel was coated with a manganese phosphate solution using the optimum conditions recommended in references 3 and 4. The coatings consisted of mixed secondary and tertiary phosphates of iron and manganese. They were smooth in appearance and dark gray in color.

Coating of the S-816 alloy (20 percent Cr, 20 percent Ni, 44 percent Co, 4 percent Mo, 4 percent W, 4 percent Nb, 3 percent Fe, and 0.4 percent C) was not possible with the solutions used for mild steel; therefore, an anodizing method was developed. The specimens were cleaned in an alkali cleaner and then anodized in a very dilute solution of orthophosphoric acid (adjusted to a pH of 2.0) using a current density of 150 milliamperes per square inch. A large cylinder of AISI 347 stainless steel was used as the cathode. Coatings were applied with thicknesses up to 1.5 mils. A chemical analysis of a typical coating is presented in table I. Iron, cobalt, and nickel were probably present as hydrated secondary and tertiary phosphates; chromium, as the hydrated tertiary phosphate; and tungsten and molybdenum, as oxides.

The thicknesses of the coatings were obtained by plating the coatings with nickel, cross-sectioning and polishing, and measuring with a microscope. The coatings on mild steel were difficult to measure quantitatively by this method, but those on the S-816 alloy could be obtained accurately.

Experimental Arrangement

A nonluminous, natural-gas - forced-air flame was employed as a flame environment. Figure 1 is a photograph of the specimens mounted in the flame. The burner was of the flat-flame type used for bending glass tubing. This type burner gives a flame having a constant temperature in a horizontal plane. The gas and air lines were fitted with sensitive pressure regulators (the pressure regulator on the air line had not been installed when photograph in fig. 1 was taken) that maintained a constant gas-air mixture when set. As a result, the temperature of the flame could be maintained constant within better than $\pm 5^{\circ}$ F during an experiment and reproduced on different days with the same precision.

The burner was operated with excess air. Under these conditions hydroxyl radicals (ref. 1, pp. 39-40) and oxygen atoms (ref. 5) have been shown to be present in the outer cone of flames of burning hydrocarbons. In addition, large numbers of hydrogen atoms must also be present (ref. 6). The specimens were situated in the outer cone, just above the inner cones.

The specimens were in the form of small cylinders, 0.250 inch in diameter and 0.375 inch long, with a thermocouple hole, 0.070 inch in diameter by 0.250 inch deep, drilled into one end along the axis of the cylinder. The specimens were supported on short lengths of small-diameter (0.065 in.) porcelain thermocouple-insulating tubing. The smaller tubes were cemented into larger tubes that were clamped rigidly to a heavy ring stand. The temperatures of the specimens were indicated by small-diameter (0.010 in.) platinum - platinum-rhodium (13 percent) thermocouples.

The specimens were placed in the flame two at a time, one coated and one uncoated; and the temperature of each was measured with a thermocouple potentiometer. Before the specimens were placed on the thermocouples, the positions of the thermocouples in the flame were carefully adjusted to give identical temperatures. The validity of the results was frequently checked by exchanging specimens on the thermocouples. The specimens were placed fairly far apart in the flame since preliminary measurements indicated there was considerable exchange of radiant energy between specimens placed side by side.

Results

Results obtained with SAE 1020 mild steel are presented in figure 2. The temperature attained in the flame is plotted against the time for an uncoated specimen and for two phosphated specimens with different coating thicknesses. These data are typical of a large number of experiments. Similar results with S-816 alloy are presented in figure 3; data are given for an uncoated specimen and for several phosphated specimens with coatings of different thickness. Also the spectral emittances are given along some of the curves.

In figure 4 is shown a cross plot of the temperature of the S-816 alloy specimens as a function of the thickness of the phosphate coating after 1 hour in the flame. Similar curves are obtained for longer periods of time in the flame.

It is evident from the data of figures 2 to 4 that, compared with the uncoated specimens, the phosphate coating effects as much as a 200°F temperature lowering in the case of the mild steel and about a 100°F lowering for the S-816 alloy (if the coating is thicker than 0.4 mil).

Experiments were conducted to ascertain the permanence of this temperature lowering, and figure 5 shows the difference in temperature between an uncoated S-816 alloy specimen and an S-816 alloy specimen with a 1-mil-thick phosphate coating. The experiment was continued for over 300 hours, and the uncoated specimens were replaced occasionally. It is evident that the temperature difference is maintained throughout the experiment.

Chemical analyses were made of the phosphate coating as formed and after exposure in the flame for periods up to 50 hours. The analyses indicated that the phosphorous either did not burn out of the coating or burned out very slowly. Exact interpretation of the analyses is not possible because of constitutional changes occurring in the coating during heating and because of increases in thickness due to oxidation of the metal underneath.

MECHANISM OF TEMPERATURE LOWERING

For an explanation of the observed temperature lowering, the ways in which heat may be gained and lost by the specimens in the flame must be considered. As the flame is nonluminous, heat is gained primarily by forced convection from the hot gases. Some is gained by absorption of the radiation emitted by the water and carbon dioxide molecules in the gas. It may also be assumed that some heat is being gained by surface recombination and reaction, as discussed in the INTRODUCTION. Heat is lost almost entirely by radiation from the surface of the specimens.

Very little is lost by conduction along the porcelain support and thermocouple wires, since both are of small diameter and extend through the flame a short distance after coming out of the specimens. Consequently, the temperature of the specimens could be lowered only by a poisoning action of the phosphorous upon the heterogeneous reactions occurring on the specimen surface or by the phosphate coating having a greater emittance¹ than the coating formed on the uncoated specimen in the flame. It is desirable to determine the relative importance of these two mechanisms. The experiments described subsequently were performed for this purpose.

Measurement of Spectral Emittances

The importance of the emittance of the surface could be ascertained by measuring the total emittance directly. However, such measurements require complex and delicate equipment. On the other hand, the spectral emittance can be measured easily with commercial equipment. And since the spectral emittance is roughly proportional to the total emittance, spectral emittances of various specimens were measured.

The measurements were made by placing the specimens on the same thermocouple at different times. The position of this thermocouple in the flame was rigidly fixed and maintained throughout all experiments. The temperature of the flame was checked before each experiment with a heavily phosphated specimen of S-816 alloy that had been burned in the flame several hours. The temperature indicated by this specimen was reproducible to $\pm 5^{\circ}\text{F}$ over the entire series of experiments.

A Leeds and Northrup optical pyrometer employing the 0.66-micron band in the red was used to measure the apparent optical temperature of the specimens. The thermocouple temperature was assumed to be the true temperature of the specimens, and the spectral emittance was calculated with the equation (ref. 8):

$$\frac{1}{T} - \frac{1}{T_s} = \frac{0.66 \times 10^{-4}}{1.438} \ln \epsilon'_\lambda$$

where T is the true temperature, T_s is the apparent temperature measured with the optical pyrometer, and ϵ'_λ is the spectral emittance.

¹Emittance is used throughout this report in preference to emissivity in conformity with the definitions of reference 7. Emissivity is considered as a property of the material and is applied only to an opaque body of the material with a polished surface; emittance is considered as a property of a body rather than the material composing it.

Actually there seemed to be slight conduction of heat from the flame along the porcelain support to the thermocouple junction so that the thermocouple indicated a slightly high temperature. Consequently, the calculated values of spectral emittance ϵ'_λ are probably low. Nevertheless, the relative values of the spectral emittances of the different surfaces are in the correct order, since all measurements were made with the same arrangement.

Results with mild-steel specimens. - Results of the temperatures attained in the flame as functions of time for three uncoated specimens with different surface treatments are presented in figure 6. Also shown is the effect of removing the flame for 5 minutes and then replacing it (the intervals out of the flame are denoted by the dotted lines). The spectral emittances for the different surfaces are given along the curves.

The temperatures of the uncoated specimens remained fairly constant as did the spectral emittances. This is probably caused by the partial pressure of oxygen in the flame being too low to oxidize the steel to any great extent in the presence of reducing gases like hydrogen, carbon monoxide, and so forth. Comparison of the spectral emittances and the temperatures of these specimens, and of the phosphated specimens as well (fig. 2), leads to the conclusion that the higher the spectral emittance of a specimen, the lower its temperature in the flame.

The behavior of the uncoated specimens upon removing the flame and replacing it corroborates this conclusion. When the flame is removed, the hot specimen is oxidized in the air while cooling; and the emittance increases. Upon replacing the specimen in the flame with this higher emittance, the temperature attained is lower; in fact, the temperature is about the same as that of the phosphated specimens. After about 30 minutes in the flame this thin oxide layer is reduced, spots of lower emittance begin to appear, and the temperature of the specimen begins to rise. The values of the spectral emittances support this explanation.

Results with S-816 alloy. - Values of the spectral emittance for the uncoated S-816 alloy specimen after various periods of time in the flame are given in figure 3. The spectral emittance is not constant as with the mild steel, but increases with time to a maximum value. Concomitantly, the temperature decreases, in harmony with the conclusion that the higher the emittance the lower the temperature. The increase in spectral emittance with time is probably caused by oxidation of the chromium in the alloy (chromium will oxidize under a much lower partial pressure of oxygen than will iron). This is supported by the

fact that upon removing the specimen from the flame for 5 minutes and then replacing, it reattains the temperature it exhibited before removal.

Spectral emittances of the phosphated S-816 specimens were all in the range 0.85 to 0.90. But no relation between spectral emittance and coating thickness was evident, because at these high values the emittance becomes more sensitive to inaccuracies in the temperature readings and the error is comparable to the range of the values.

One would expect that the total emittance would increase rapidly at first with increasing coating thickness and level off to a constant value (ref. 9). If the temperature is determined by the total emittance, a plot of temperature against coating thickness should resemble that of figure 4.

On the other hand, if the temperature lowering is a result of surface poisoning, it should be independent of coating thickness. Hence, these results also indicate that the temperature lowering observed arises mainly from the phosphate surface having a greater total emittance than the uncoated surface.

Comparison with Surfaces of Known Total Emittance

Specimens were made from Nimonic 80 and Inconel. The surfaces were roughened by sandblasting and blackened by oxidation for 1/2 hour at 2100° F for Inconel and 2300° F for Nimonic 80. The total emittances of surfaces so treated have been measured (refs. 9 and 10) and are close to 1. It was anticipated that, if the temperatures of these specimens in the flame were considerably higher than the phosphated S-816 alloy, then some poisoning action must be involved in the case of the phosphate coating.

A specimen coated with the National Bureau of Standards (NBS) ceramic coating A-418 was also included. The total emittance of this surface has been measured (ref. 10).

The measurements were made employing the same procedure used to measure the spectral emittances; namely, all specimens were placed on the same thermocouple, flame temperature was checked with heavily phosphated S-816 specimen, and so forth.

The temperatures attained by different specimens in the flame along with the value of the total emittance of their surface are given in table II. The results presented are averages of several specimens, except for the NBS coating. Individual specimens of any given type varied $\pm 5^\circ$ F in their temperature.

The data indicate the same relation between specimen temperature and total emittance as did the results described previously. The pre-oxidized Nimonic 80 attained a temperature about the same as that of the phosphated S-816 alloy. This result indicates that the lowering effected by the phosphate coating could be explained by assuming a total emittance of 1 for the surface. Since the surface of a specimen is both roughened and blackened by phosphating, this assumption is not unlikely.

Measurement of Poisoning Effectiveness of Surfaces

If heat is being gained by metal surfaces exposed to flames through surface recombination of atoms, the poisoning effectiveness of a coating for the hydrogen- and oxygen-atom recombinations should be important since these atoms are the most abundant in flames. To get some idea of the poisoning effectiveness of the coatings, specimens were tested in the gas stream issuing from a low-pressure discharge tube similar to that shown in figure 7 and described in reference 11. When moist hydrogen or oxygen at a pressure of 0.5 millimeter of mercury is subjected to such a discharge, the gas issuing from the discharge tube contains a fairly high proportion of atoms, about 5 to 10 percent. These atoms will recombine readily on metal surfaces, heating the metal. For temperatures below about 800° F, the temperature rise is directly proportional to the power supplied by the atom recombination, which in turn is proportional to the number of atoms recombining per second. Thus, the temperature rise gives a measure of the number of atoms recombining per second. If the metal surface is now poisoned by some coating, fewer of the atoms striking the surface will recombine; and the temperature rise will be smaller. Hence, the temperature rise of a metal specimen when coated compared with the rise when uncoated, for a given set of operating conditions, gives an approximate measure of the poisoning effectiveness of the coating. The poisoning effectivenesses of phosphate coatings on S-816 alloy specimens were evaluated in this way.

The specimens were hollow cylinders closed on one end. They were 0.375 inch long with an inside diameter of 0.155 inch and a wall thickness of 0.005 inch. For an experiment, the specimen was fitted snugly over the closed end of a glass tube that was 0.153 inch in diameter and about 3 feet long. An iron-constantan thermocouple was pressed against the inside of the closed end of this glass tube and was used to measure the temperature rise of the specimen. The glass tube was mounted in an O-ring slip seal so that the distance of the specimen from the discharge tube could be adjusted (see fig. 7).

A series of specimens were tested in a hydrogen-atom stream and also in an oxygen-atom stream (a small fraction of OH radicals was also present because of the water content). The results are presented in table III.

For the first three specimens, which were phosphated, the ratio of the temperature rise when coated ΔT_c to that when uncoated ΔT_u is about the same for both atoms, that is, about $2/3$. Apparently the phosphate coating decreases the temperature rise by about $1/3$. The value of $\Delta T_c/\Delta T_u$ is also shown to be independent of coating thickness by these data. Hence, the temperature lowering cannot be attributed to an insulating effect. Also, since the temperatures are low, the emittance of the surface should have little influence. Consequently, it may be concluded that the phosphate coating reduces the amount of atom recombination by about $1/3$. It was also found that exposing the phosphated specimen to the burner flame for 2 hours had no effect on the temperature rise attained in either a hydrogen- or oxygen-atom stream.

The last two specimens instead of being phosphated were placed in the flame for 2 hours. The value of $\Delta T_c/\Delta T_u$ for these was only 0.27, indicating that the coating formed in the flame had about twice the poisoning effectiveness of the phosphate coating. Therefore, if surface poisoning is important in determining the temperature of the metal specimens placed in the flame environment, the uncoated S-816 specimen should attain a lower temperature than the phosphated S-816 specimen. But the results in the flame environment presented in figure 3 show that the phosphate-coated S-816 specimen attained a temperature 100° F lower than the uncoated specimen exposed to the flame. Hence poisoning effectiveness for the hydrogen- or oxygen-atom recombination must have little to do with the temperature lowering in the flame. Therefore, this result also indicates that the temperature lowering must arise primarily from the high emittance of the phosphate coating.

CONCLUDING REMARKS

It has been shown that a phosphate coating on a metal specimen exposed to a hydrocarbon-flame environment effects a reduction in the temperature of the specimen. Results of several types of experiments indicate that the temperature lowering results from the high emittance of the phosphate coating. The emittance of the coating appears to be about 1. Such a coating might find application on the outside of combustor cans or on other airplane components where maximum heat loss by radiation is desirable.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, April 24, 1956

REFERENCES

1. Gaydon, A. G.: Spectroscopy and Combustion Theory. Second ed., Chapman and Hall (London), 1948.
2. Schwab, Georg-Maria, Taylor, Hugh S., and Spence, R.: Catalysis. D. Van Nostrand Co., Inc., 1937.
3. Macchia, O.: Die mangelhaften Phosphatüberzüge, deren Ursachen und Abhilfe. Korrosion und Metallschutz, Jahrg. 12, Nr. 8, 1936, pp. 211-219.
4. Holden, H. A.: Chemical and Electrochemical Factors Influencing the Formation of Phosphate Coatings. Jour. Electrodep. Tech. Soc., vol. XIX, 1943-1944, pp. 23-33.
5. Gaydon, A. G.: Continuous Spectra in Flames: The Role of Atomic Oxygen in Combustion. Proc. Roy. Soc. (London), ser. A, vol. 183, no. A 992, Aug. 10, 1944, pp. 111-124.
6. Kondratieva, H., and Kondratieva, V.: Detection and Measurement of the Concentration of Hydrogen Atoms in Hydrogen Flame. Acta Physiochim. (U.R.S.S.), vol. XXI, no. 1, 1946, pp. 1-12.
7. Worthing, A. G.: Temperature Radiation Emissivities and Emittances. Temperature—Its Measurement and Control in Science and Industry, Reinhold Pub. Corp., 1941, pp. 1164-1187.
8. Smithells, Colin J.: Metals Reference Book. Interscience Pub., Inc., 1949, p. 466.
9. Sully, A. H., Brandes, E. A., and Waterhouse, R. B.: Radiation Suppressing Coatings for Metals at Elevated Temperatures. Special Rep. No. 1, Fulmer Res. Inst., Apr. 1953.
10. De Corso, S. Mario, and Coit, Roland L.: Measurement of Total Emissivities of Gas-Turbine Combustor Materials. Paper No. 54-SA-26, A.S.M.E., June 1954.
11. Fryburg, George C.: Enhanced Oxidation of Platinum in Activated Oxygen. Jour. Chem. Phys., vol. 24, no. 2, Feb. 1956, pp. 175-180; discussion, p. 180.

TABLE I. - CHEMICAL ANALYSIS OF
TYPICAL COATING ON S-816 ALLOY

Element	Percent ^a
P	8.3
Fe	8.2
Co	2.0
Ni	1.2
W	4.0
Mo	3.0
Cr	5.8

^aBalance is oxygen in the
phosphate radicals and
water of hydration.

TABLE II. - TEMPERATURES ATTAINED BY DIFFERENT SPECIMENS

IN FLAME ENVIRONMENT

Surface condition	Specimen temperature, °F	Temperature difference ^a , °F	Total emittance
Phosphate coat on S-816 alloy ^b	1645	0	
National Bureau of Standards coating A-418 on S-816 alloy ^c	1700	55	^d 0.87
Roughened and preoxidized Inconel ^e	1690	45	^d .94
Roughened and preoxidized Nimonic 80 ^f	1645	0	^g 1

^aCompared to phosphated S-816 alloy.

^bCoating about 1-mil thick.

^cCoating about 1-mil thick; fired at 1875° F. Supplied by Dr. D. G. Moore of National Bureau of Standards.

^dRef. 10.

^eOxidized in air for 1/2 hour at 2100° F. Surface sandblasted prior to oxidation.

^fOxidized in air for 1/2 hour at 2300° F. Surface sandblasted prior to oxidation.

^gRef. 9. Nimonic 80 and Nimonic 75 assumed to behave similarly.

TABLE III. - POISONING EFFECTIVENESS OF DIFFERENT SURFACES AS
DETERMINED BY TEMPERATURE RISE IN ACTIVATED GASES

Specimen type and number	Gas	Temperature rise for clean surface, ΔT_u , $^{\circ}\text{F}$	Temperature rise after coating, ΔT_c , $^{\circ}\text{F}$	Thickness of coating, mils	$\Delta T_c/\Delta T_u$
S-816 alloy (no. 1)	Moist H_2	327	220	0.5	0.67
S-816 alloy (no. 3)	Moist O_2	378	243	1.1	.65
S-816 alloy (no. 8)	Moist O_2	279	185	.3	.66
S-816 alloy (no. 9)	Moist O_2	292	74	Oxidized in flame for 2 hr	.25
S-816 alloy (no. 10)	Moist H_2	302	81	Oxidized in flame for 2 hr	.27

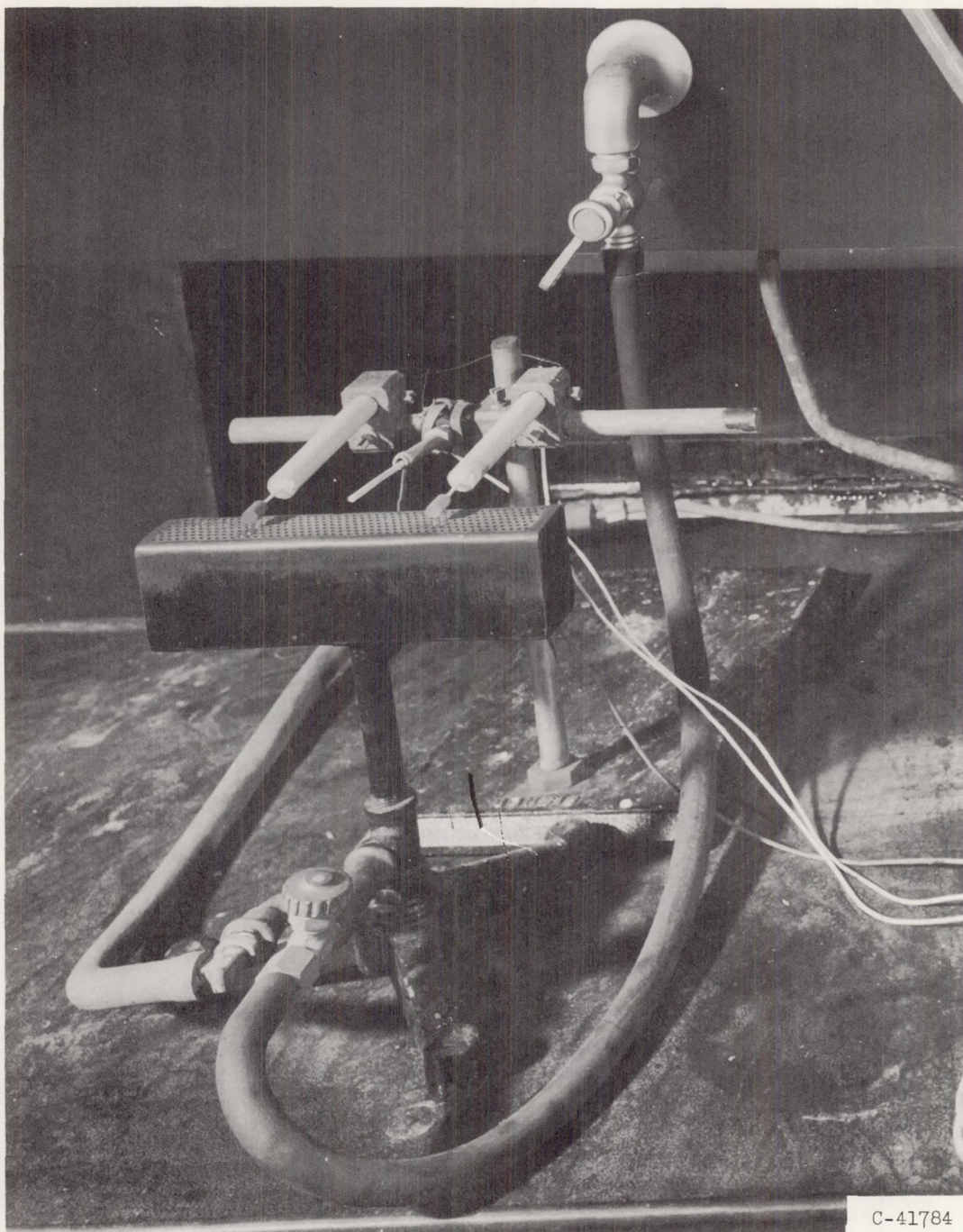


Figure 1. - Specimens mounted in flame.

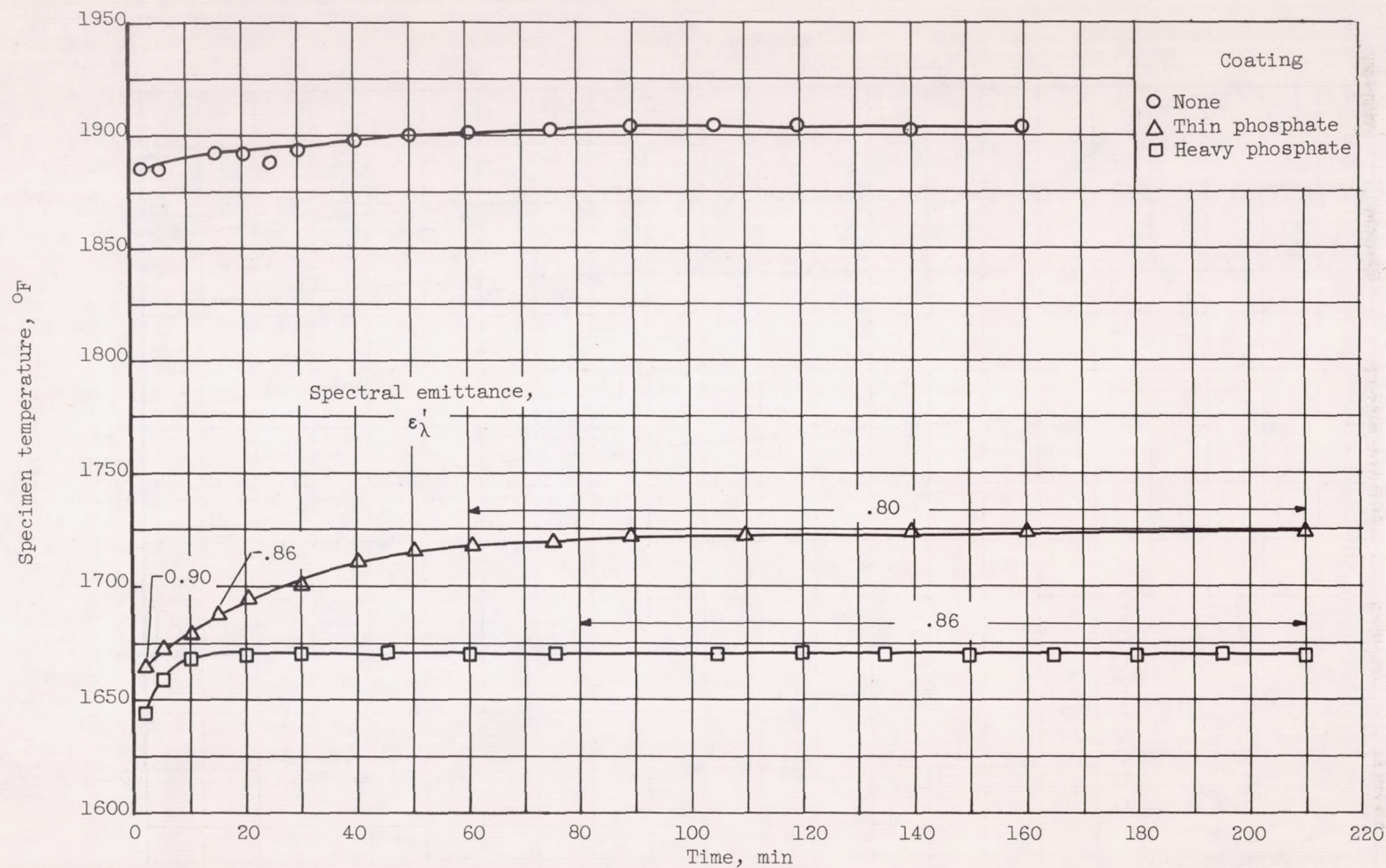


Figure 2. - Temperatures of one uncoated specimen and two phosphate-coated specimens of SAE 1020 mild steel in flame environment.

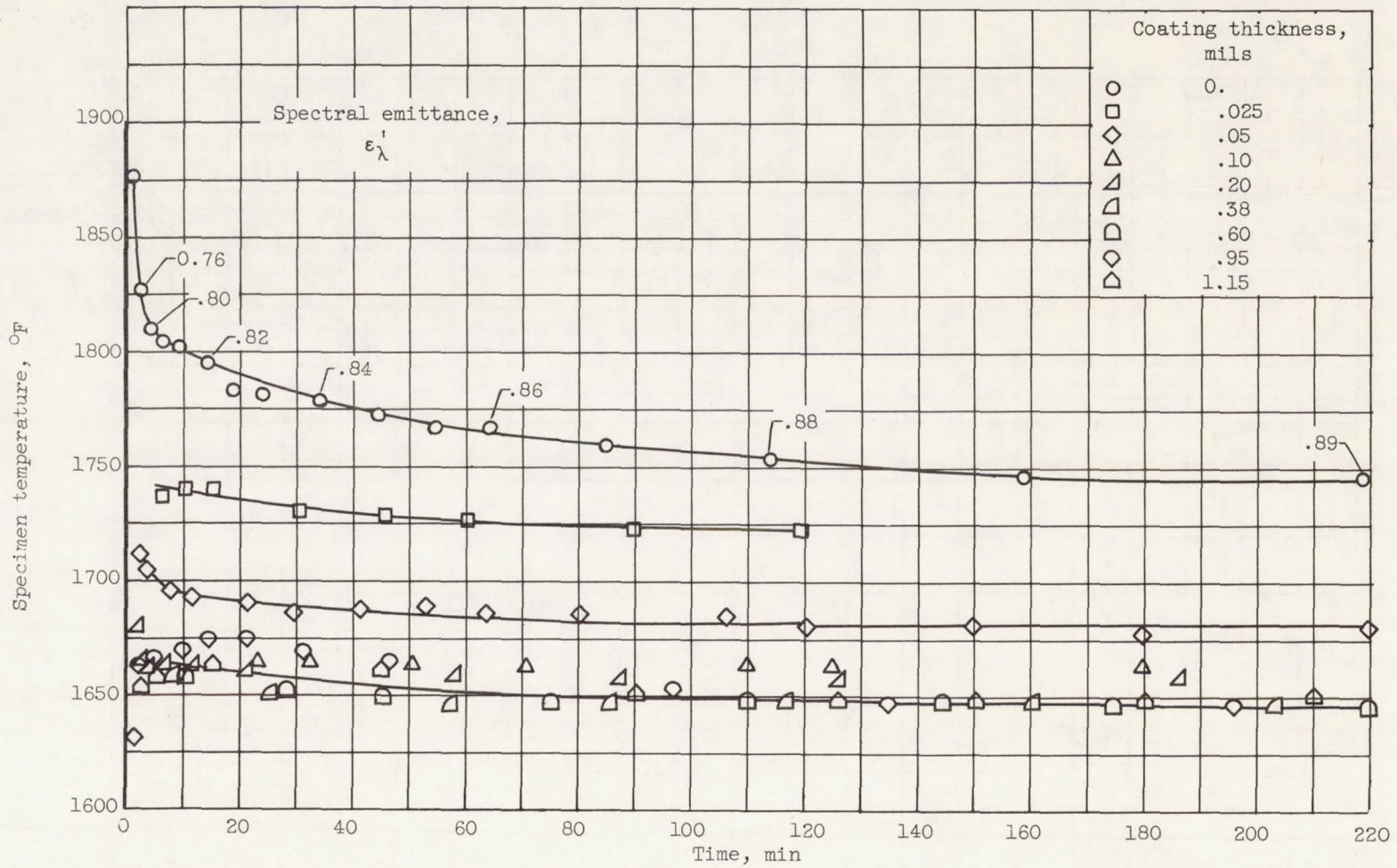


Figure 3. - Temperatures of one uncoated specimen and several phosphate-coated specimens of S-816 alloy.

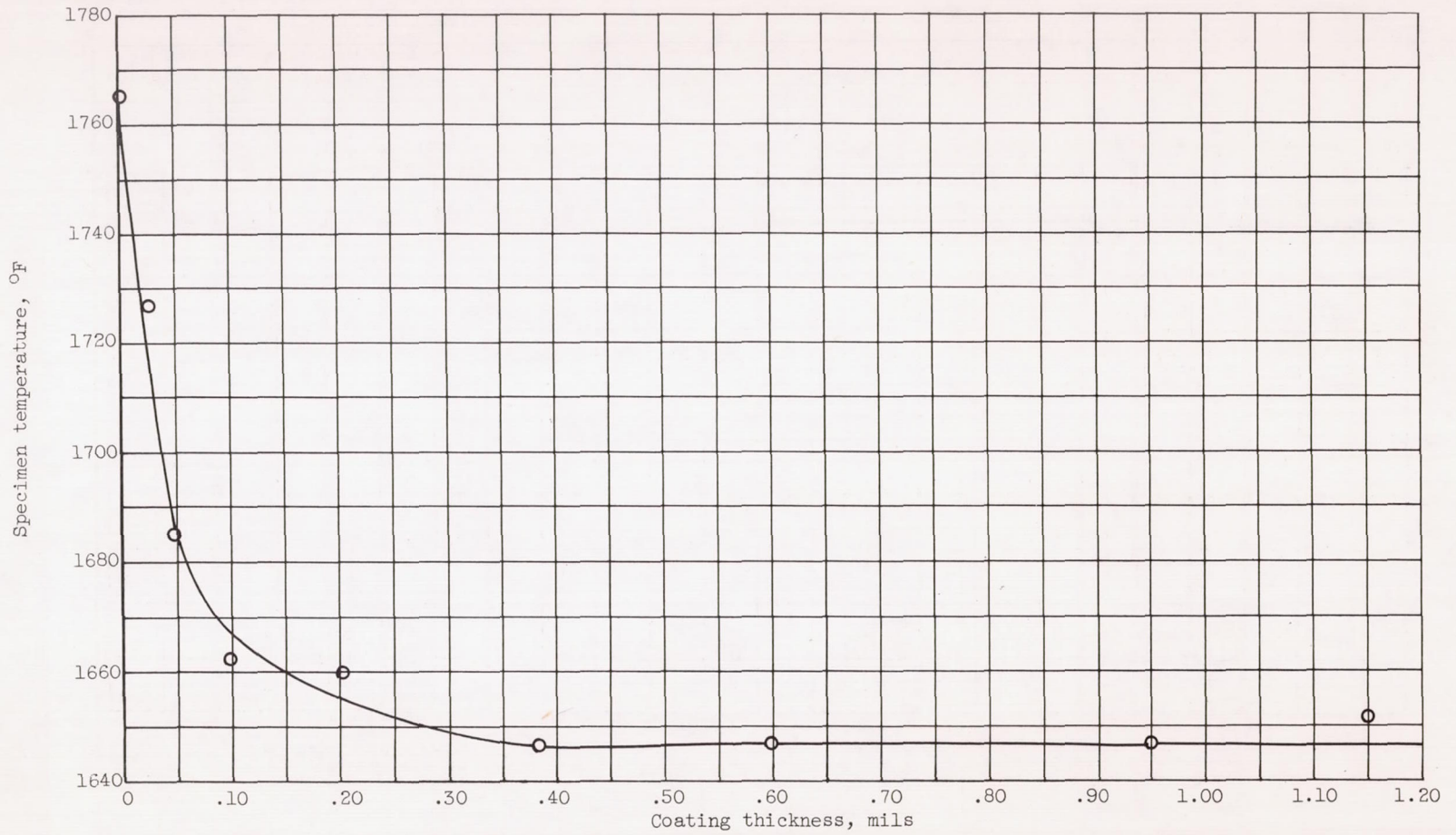


Figure 4. - Effect of thickness of phosphate coating on temperature of S-816 alloy specimens.

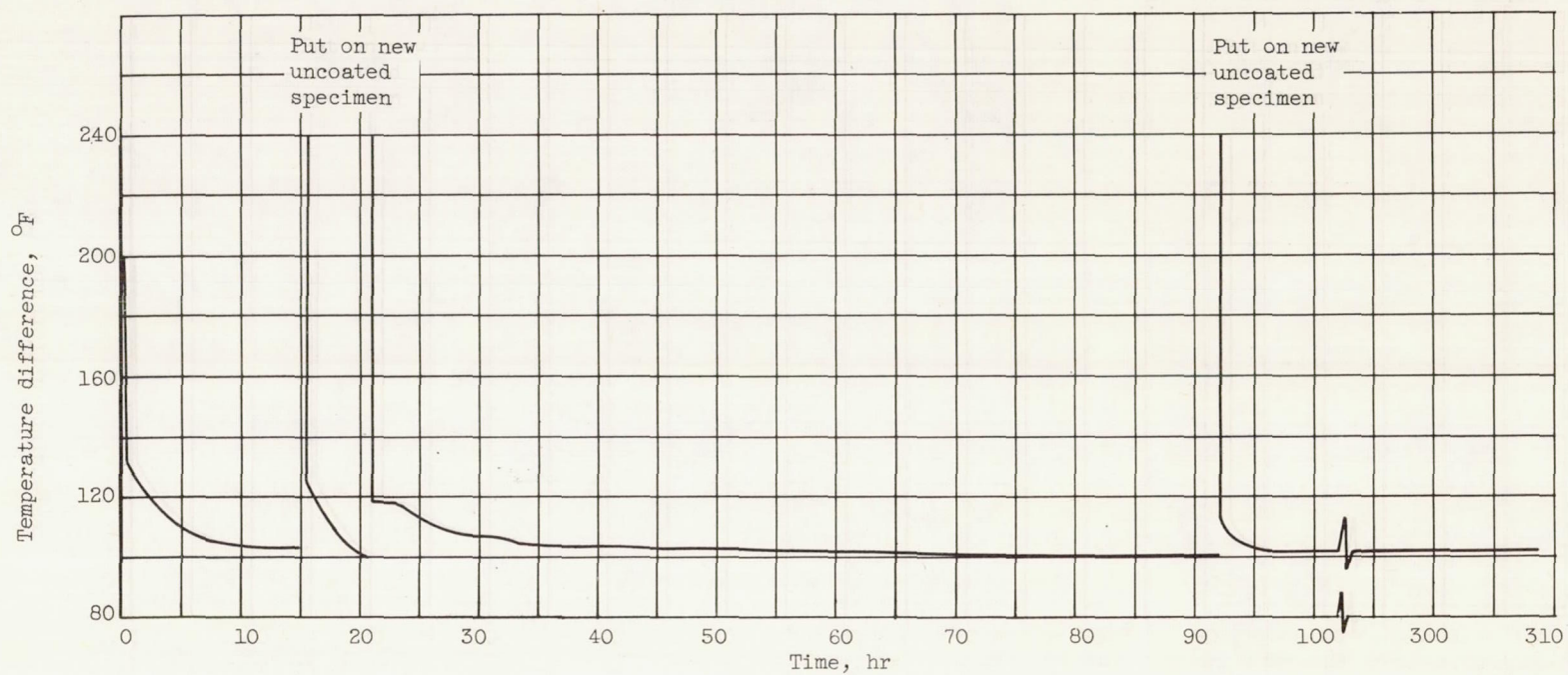


Figure 5. - Temperature difference between phosphate-coated and uncoated S-816 alloy specimens in flame environment.
Phosphate-coating thickness, 1 mil.

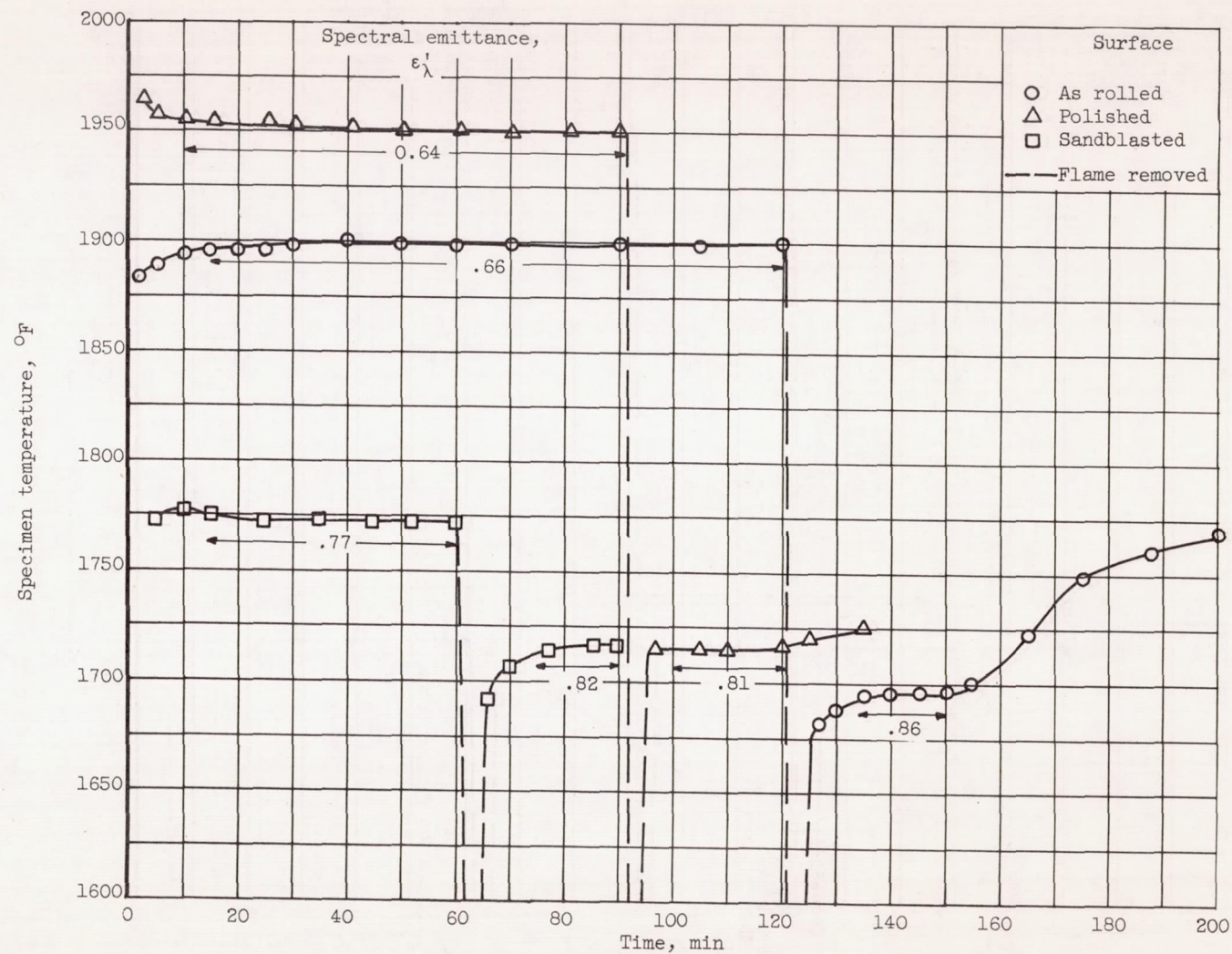


Figure 6. - Temperatures of uncoated mild-steel specimens with different surface treatments.

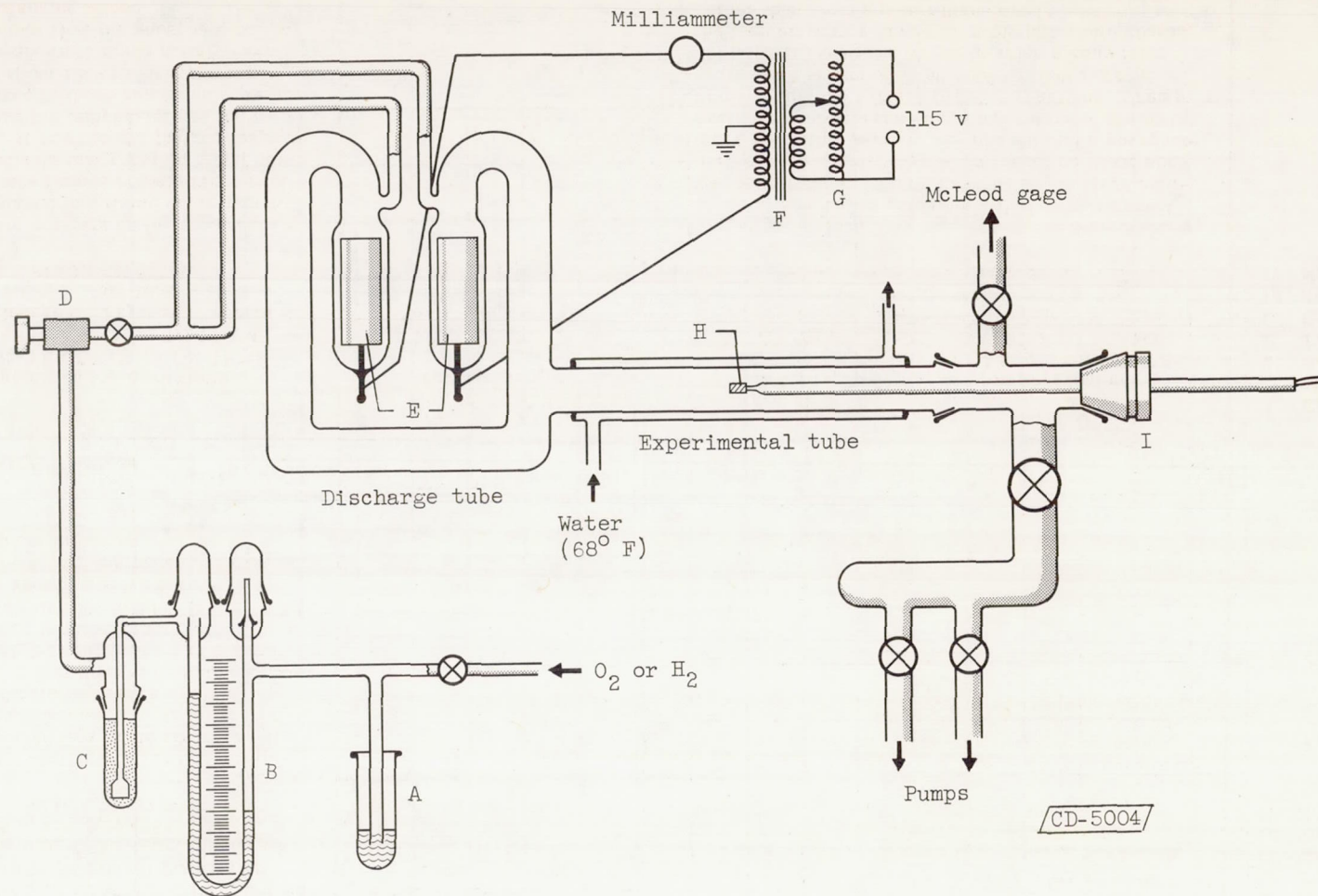


Figure 7. - Apparatus for producing activated gases: A, Octoil manostat; B, Octoil flowmeter; C, water saturator with porous-glass bubbler; D, Hoke vacuum needle valve; E, hollow cylindrical electrodes of 2-SO aluminum mounted on tungsten lead-ins; F, 15-kilovolt transformer; G, Variac; H, specimen; I, tapered brass plug with O-ring slip seal.